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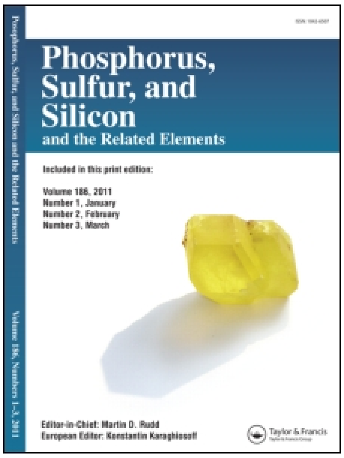

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Synthesis and Reactivity of New Silylated Sulfur-Containing Heterocyles Through Thionation of Bis(Acylsilanes)

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*The optimization of the synthesis of 2,6-bis(trialkylsilyl)4*H*-thiopyranes and some aspects of the reactivity of the corresponding lithium salts with alkyl halides and benzaldehyde are presented.*

Keywords Acylsilanes; heterocycles; thiopyranes

Acylsilanes are well-known versatile compounds that act as intermediates in synthetic organic chemistry. Only recently bis(acylsilanes) **1** have been investigated and have been demonstrated as very useful molecules able to participate in a number of interesting reactions.[1] On the other hand, the use of a hexamethyldisilathiane (HMDST)/

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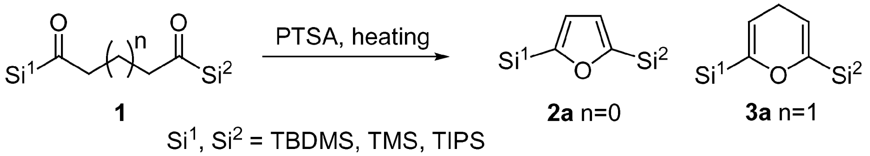
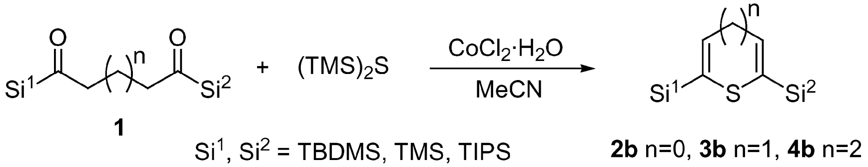
$CoCl_2 \cdot 6H_2O$-based procedure has proved to be mild and efficient in thionating acylsilanes and acylstannanes.[2]

Bis(acylsilanes) are known to cyclize in an acidic medium to lead to unsaturated oxygenated heterocycles like 2,5-bis(trialkylsilyl)furanes **2a** or 2,6-bis-trialkylsilanyl-4*H*-pyranes **3a**, depending on the length of the spacer between the two silylcarbonyl functionalities[3] (Scheme 1).



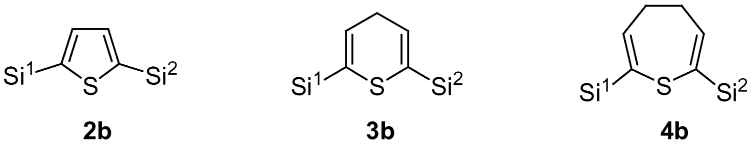
SCHEME 1

The reaction with HMDST in a mild acidic medium using the $CoCl_2 \cdot 6H_2O$ catalyst leads to new bis-silylated sulfur-containing heterocycles **2b–4b**[4] (Scheme 2).



SCHEME 2

This new synthetic procedure represents an alternative way to prepare molecules such as symmetrical and unsymmetrical 2,5-bis-trialkylsilyl-thiophenes[5] **2b** and is currently the only way to synthesize molecules such as symmetrical and unsymmetrical 2,6-bis-trialkylsilyl-4*H*-thiopyranes **3b** and 2,7-bis-trialkylsilyl-4,5-dihydro thiepines **4b** (Scheme 3).



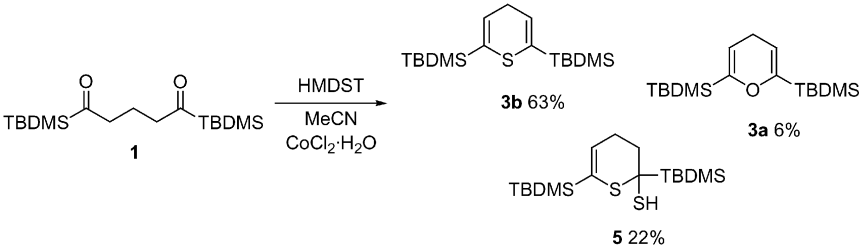
SCHEME 3

We report here the optimization of preparation of 2,6-bis(trialkylsilyl)-4*H*-thiopyranes **3b** and some aspects of their reactivity.

RESULTS

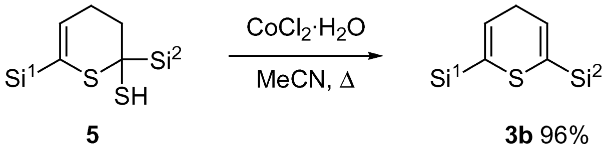
Optimization

The preliminary reported (HMDST)/$CoCl_2 \cdot 6H_2O$ thionation procedure led to a mixture of coumpounds: 2,6-bis(trialkylsilyl)-4*H*-pyranes **3a** and the thiolic intermediate **5** were present in the reaction mixture along with the expected compound **3b** (Scheme 4).



SCHEME 4

The amount of the oxygenated heterocycle **3a** can be reduced by carrying out the reaction at 0°C and adding the catalyst, ($CoCl_2 \cdot 6H_2O$), portionwise. Furthermore, the isolated thiol intermediate **5** could in turn be converted into the desired compound **3b** by reacting with $CoCl_2 \cdot 6H_2O$ in refluxing MeCN (Scheme 5).



SCHEME 5

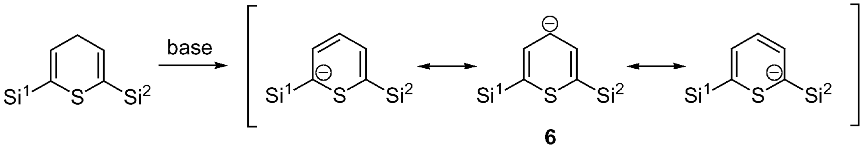
Further studies are ongoing to avoid the formation of the oxygenated compound **3a** and the isolation of **5** prior to its conversion into the final compound **3b**.

Reactivity

The reactivity of the symmetrical and unsymmetrical 4*H*-thiopyranes **3b** has been studied. Reactions of alkylation on the sulfur atom using different alkyl halides did not lead to any alkylation products even using catalysts like silver salts.[6]

Oxidation tests using peracids in the same conditions used to oxidize **2b** to the corresponding sulfone[7] led to degradation of the starting material and to a complex mixture.

When 2,6-bis(trialkylsilyl)4*H*-thiopyranes **3b** were treated with strong bases, a deep red color developed in the reaction medium because of the formation of the corresponding highly conjugated carbanion **6** (Scheme 6).

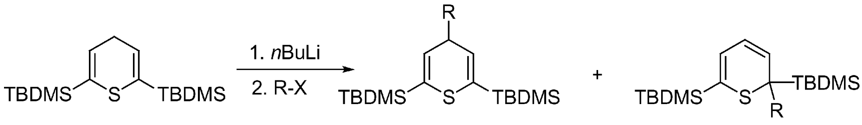


6

SCHEME 6

Nucleophilic substitution and addition were explored, focusing our attention on the chemo- and regioselectivity aspects. Reaction with alkyl halides could, in principle, lead to alkylation of the positions 2 and 4 of the heterocyclic ring in the case of symmetrical compound or 2, 4, and 6 in the case of unsymmetrical one; furthermore, reactions with carbonyl compound could lead to alcohol by reaction from position 4 or to a Peterson-type reaction by reaction from positions 2 and 6.

It was found in the reaction of the symmetrical substrate **7** with alkyl halides that coupling occurred at positions 2 and 4 of the heterocyclic ring with a ratio that depends on the nature of the electrophile (Scheme 7 and Table I). The unsymmetrical compound **10** reacts similarly, with no significant difference in regioselectivity.

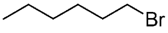
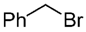
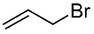
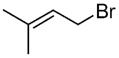


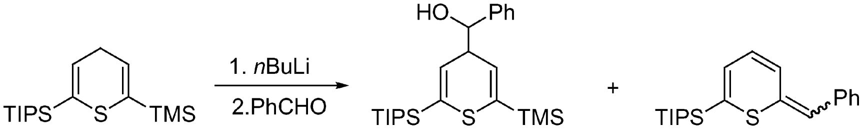
7 **8** **9**

SCHEME 7

Although the trapping of the carbanion with alkyl halides gives 2- and 4-alkyl-2,6-bis(trialkylsilyl)4*H*-thiopyrane, whatever the silyl substituents, the reactions with carbonyl compounds depends on the substitution pattern. Reaction of the lithio derivative of **10** with benzaldehyde leads to the alcohol **11** and to (6-benzylidene-6*H*-thiopyran-2-yl)-tris(isopropyl)silane **12** as a result of a Peterson-type reaction (Scheme 8). In the same conditions, the bis(TBDMS) derivative **7** is converted selectively into the 4-substituted adduct.

TABLE I

R-X	**8** (%)	**9** (%)
MeI	>98	–
	44	6
	46	10
	35	63
	33	6



10 **11** 65% **12** 22%

SCHEME 8

Studies are underway to optimize the chemo- and regioselectivities of these processes.

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